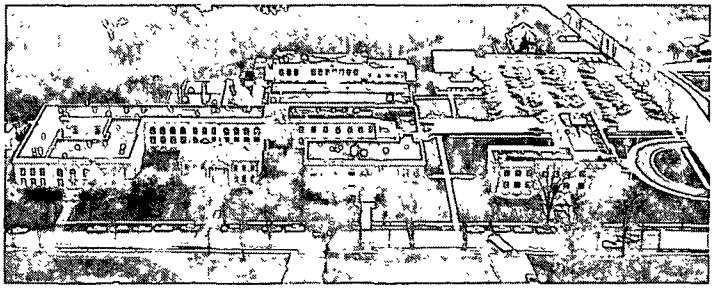

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OXYGEN DELIGNIFICATION

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OXYGEN DELIGNIFICATION

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ABSTRACT

This paper reviews the technology for delignifying unbleached pulps with oxygen in both high consistency and medium consistency processes. Fundamental chemical and physical features common to both are first briefly considered. These include chemical aspects of the reactions of lignin and carbohydrates with oxygen, the related concept of selectivity and ways to control it, kinetics, mass transfer, and heat effects. The processes and their behavior are then described within this framework. Implications of the oxygen stage for the system as a whole are also outlined. A representative sampling of the literature, including recent publications, is included.

INTRODUCTION

The development of oxygen delignification, or brownstock oxygen bleaching, has been driven by environmental, economic, and energy-related considerations (1-6). The environmental benefits include substantial reductions in bleach plant effluent BOD, color and organic chlorine compounds. They are realized by removing much of the lignin in the unbleached pulp before the chlorination stage. The dissolved material, unlike that from chlorination and caustic extraction, is uncontaminated by chloride ion. It can therefore be routed back to the recovery furnace, where it becomes a source of energy instead of a pollutant.

Chemical cost savings arise from reductions in the need for chlorine, caustic and chlorine dioxide. Chemical savings in the chlorination and caustic extraction stages are proportional to the amount of lignin removed in the oxygen stage. These savings are not balanced by the cost of operating the oxygen stage itself because the source of alkali in this stage can be oxidized white liquor and the oxygen needed is cheaper than the chlorine it replaces. Chlorine dioxide savings in the later stages are presumed to be due to beneficial changes in the residual lignin structure brought about by its earlier exposure to oxygen.

Equipment cost savings can result from the easy bleachability of oxygen delignified pulp relative to raw brown stock. The number of conventional stages can often be decreased to allow "short sequence bleaching." This also reduces energy and operating costs.

Energy-related benefits include recovery of heat from the burning of the material removed from the pulp in the oxygen stage, lower refining energy requirements of oxygen bleached pulps and the fact that the manufacture of oxygen requires only about one-eighth of the energy required to make a chemically equivalent amount of chlorine.

As a result of these benefits, worldwide oxygen delignification capacity has enjoyed steady growth since its introduction in 1970, as shown in Fig. 1. There are currently approximately 45 systems in operation, producing a total of more than 25,000 tons of pulp per day.

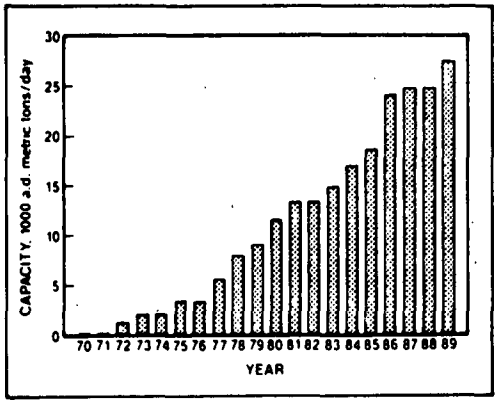

Figure 1. Worldwide production capacity of oxygen-delignified pulp (1).

FUNDAMENTALS

Two key obstacles that must be overcome in using oxygen to bleach pulp are its tendency to attack carbohydrate as well as lignin and difficulty in getting it to the reaction site within the fiber wall. Achieving high selectivity for lignin requires an understanding of certain features of the reactions of oxygen and alkali with both lignin and carbohydrates. Achieving efficient mass transfer requires recognition of some of the factors that govern mass transfer in gas-containing pulp suspensions. Good process design and operation also demands a knowledge of the stoichiometry, thermal effects and products of the reactions that occur in oxygen bleaching.

Lignin Reactions

Important reactions of lignin are initiated when a phenolic hydroxyl group in lignin reacts with alkali to form a phenolate ion. The ion then reacts with oxygen to form a reactive intermediate called a hydroperoxide. This intermediate then undergoes fragmentation by one of several possible pathways. These include reactions that break up the polymeric structure of the lignin molecule and other reactions that make the resulting fragments more water soluble (7). Lignin-derived free radicals are also formed. These may, in a counter-productive step, react with each other to increase the molecular weight of the lignin fragments, making them less soluble (8). A final important feature of the delignification process is that some of its component reactions produce hydrogen peroxide, which can further react with both lignin and carbohydrates.

Carbohydrate Reactions

Carbohydrate degradation is the chief factor limiting the amount of delignification that can be achieved in the oxygen stage. It occurs mainly by random cleavage of the chainlike cellulose molecule, which results in a reduction in chain length and manifests itself as a decrease in the viscosity of a solution of the pulp in a cellulose solvent. If allowed to proceed beyond a certain point it will also appear as a loss of pulp strength. It involves free radical processes in which peroxides and metal ions such as iron, manganese and copper play an important part (9-13).

In the presence of these ions, reactive radicals are formed that randomly attack links in the cellulose chain, resulting in chain breakage at the point of attack. This reduces pulp viscosity and, if allowed to proceed far enough, results in a loss of pulp strength. Since the attack is random, it is unlikely that it will occur close enough to the end of the chain to produce a low molecular mass, soluble fragment. This kind of reaction therefore has little or no effect on pulp yield.

The reaction by which yield is lost in alkaline medium is called the peeling reaction because it successively removes single monomeric units from the end of the cellulose chain. For an end unit to be susceptible to removal by the peeling reaction, it must contain a certain structural feature - a carbonyl group. Since peeling leaves a carbonyl group in what becomes the new end unit when the previous one is removed, it could in principle continue until all the pulp dissolved. This is prevented by the occurrence of a competing reaction called the stopping reaction that converts the end unit to one that does not contain a carbonyl group.

In the oxygen bleaching of kraft pulps, yield loss is not a serious problem, for two reasons. Kraft pulps, because of their long exposure to strongly alkaline conditions in the digester, contain very few end units that have not been converted to the stable form by the stopping reaction. The other reason is that oxygen itself converts reducing end groups to stable oxidized forms. Note, however, that peeling can be a problem if random chain cleavage is excessive, since chain cleavage creates a new chain end that contains a carbonyl group.

Selectivity

Selectivity can be loosely defined as the ratio of attack on lignin to attack on carbohydrate. Among the factors governing selectivity in oxygen bleaching, one of the most important is the transition metal ion content of the pulp, since these ions catalyze the generation of harmful radical species. Most pulps contain appreciable quantities of iron, copper and manganese, all of which have this effect. One approach to dealing with the problem is to remove the metals by acid washing prior to the oxygen stage. Another is to add comcompounds to the pulp that inhibit carbohydrate degradation. These compounds are called carbohydrate protectors.

The protector of greatest commercial importance is the magnesium ion. The discovery of its effectiveness in 1963 by Robert and co-workers (14) provided a great impetus to the development of oxygen bleaching. Since then a considerable number of compounds have been found effective, but none is as economical as magnesium. It is normally applied at levels as low as 0.05-0.1% (as Mg^{+2}, o.d. pulp basis). It is believed to function by precipitating as magnesium hydroxide, which adsorbs the metal ions, making them unavailable for catalysis of peroxide decomposition (15).

Figure 2 (5) illustrates the effectiveness of magnesium in preserving pulp viscosity and is typical of selectivities obtained in the bleaching of softwood kraft pulp.

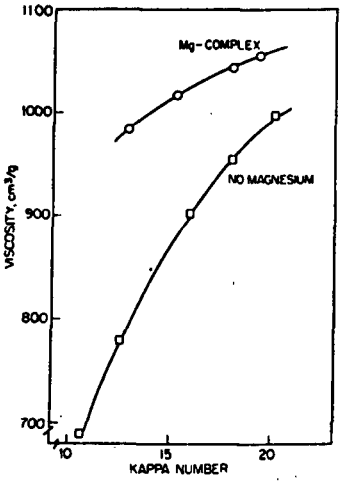

Figure 2. Effect of magnesium on selectivity in the oxygen bleaching of Scandinavian softwood kraft pulp (5).

It is apparent from the nonlinear nature of the curves in Fig. 2 that selectivity does not remain constant as the kappa number of the pulp is decreased to progressively lower levels. However, it is commonly observed to remain nearly constant until about 50% of the lignin has been removed from the pulp, and to deteriorate beyond that point. In virtually all of the existing systems the target degree of delignification is 60% or less. When it is limited to 45-50%, the resulting pulp may be fully bleached to give a final product of quality equivalent to the corresponding conventionally bleached pulp, although its viscosity is usually slightly lower.

Although not as yet commercialized, selectivity improvement by nitrogen dioxide pretreatment is a potentially significant development. Pioneered by Yethon (16), this process has been intensively studied and developed by Samuelson and co-workers (17,18). Treatment of unbleached kraft pulp with nitrogen dioxide in the presence of oxygen makes a subsequent oxygen stage more selective and efficient, even when the conditions of the oxygen stage are mild. Lignin removal in the oxygen stage can be increased to 80%, considerably enhancing pollution abatement benefits. The process has reached the pilot plant stage (19), where some problems associated with recycling an acid effluent remain to be solved.

Other pretreatments have also been shown to favorably affect oxygen stage selectivity (20). These include chlorine, chlorine dioxide and acidic hydrogen peroxide.

Mass Transfer

Mass transfer is an important consideration because most oxygen bleaching systems have all three phases present. Oxygen must cross the gas-liquid interface, diffuse through the liquid film surrounding the fiber, and finally diffuse into the fiber wall before reacting. Depending on the conditions, the rate of oxygen transport can limit the rate of the overall process, because of the inherent slowness of the diffusion phenomena involved (21).

The mass transfer problem is aggravated by the low solubility of oxygen in aqueous sodium hydroxide (22,23). Typically, bleaching at 15% consistency consumes 24 times as much oxygen as can be present in the liquid phase at any one time, and at 27% consistency, 50 times as much. A viable process must obviously facilitate the transfer of oxygen into and through the liquid phase. This can be done by ensuring that the partial pressure of oxygen in the gas phase and the gas-liquid interfacial area are both sufficiently large.

Kinetics

Several studies have examined the dependence of the rates of the delignification and carbohydrate degradation reactions on reactant concentrations and temperature (24,25). The lignin in the pulp appears to be of two different types which differ with respect to the ease of their removal by oxygen. The first type is removed within about the first 10 minutes in a rapid initial phase. Removal of the second type proceeds at a rate that is proportional to the amount remaining, which means that the lignin content can be reduced to any desired level by allowing the reaction to continue for a long enough time. In practice, this is not normally observed because the extent of reaction is limited by the availability of alkali. The rates of removal of both types of lignin increase with increases in alkali concentration, oxygen partial pressure and temperature.

Depending on reactor type and reactor conditions, the rate of delignification may be determined either by the intrinsic chemical reaction rate or by the rate of mass transfer of oxygen or alkali to the fiber. In the limiting case, where mixing is so good that oxygen and alkali are equally available to all fibers, the rate is equal to the chemical reaction rate. Empirical models are available for predicting this rate, and can be used to evaluate the mixing in a given reactor (26). They indicate that high shear mixers are capable of achieving very good mixing of alkali and oxygen with pulp at medium consistency.

Heat Effects

At reasonable alkali levels, temperatures in the range 100-130°C are needed, and consideration must be given to adding and recycling the required amount of heat, especially in medium and low-consistency processes. The heat of reaction is appreciable (27) and its removal may be a problem in high-consistency, high kappa-drop systems.

Chemical Consumption

The stoichiometry of oxygen bleaching is such that, for each unit of kappa number reduction, about 0.1-0.13% NaOH (o.d. pulp basis) and a similar amount of oxygen are required. In high consistency systems, alkali consumptions in this range are realized in practice. Medium consistency systems tend to consume slightly more alkali, because its concentration is lower at a given charge in these systems. Oxygen consumptions are usually somewhat higher than theoretical because of losses due to reactor venting or entrainment with the pulp leaving the reactor.

Reaction Products

Reaction products include organic acids and carbon dioxide, small amounts of carbon monoxide, and traces of methanol. Since the last two are combustible, their concentrations in the gas phase of high consistency reactors must be controlled for safety reasons. This can be accomplished either by continuously bleeding gas from the reactor or by circulating it through a catalytic converter.

THE HIGH CONSISTENCY PROCESS

One approach to solving the three-phase mass-transfer problem is to remove most of the free liquid phase. This has the twofold effect of providing a very large gas-liquid interfacial area and reducing the thickness of the liquid layer through which oxygen must diffuse to reach the fiber. Also, the amount of recycled, potentially oxidizable dissolved organic material in the reactor is reduced, as is the amount of water which needs to be heated to the reaction temperature.

For these reasons, many of the existing commercial installations operate at high consistency. Two systems are available: the Sapoxal process, marketed by Kamyr, and the MoDo-CIL process, marketed by MoDo Chemetics. The two are fairly similar, the only major difference being in the design of the reactor itself.

The MoDo-CIL process (30-34) uses a vertical cylindrical reactor designed to contain a continuous pulp bed at a consistency of about 27% (Fig. 3). Keeping the consistency at or slightly above this value prevents bed compaction, which would otherwise reduce the free volume needed to serve as an oxygen reservoir. Feeding is by a screw feeder or thick stock pump, which maintains a seal against the reactor pressure. At the bottom of the reactor the pulp is diluted to 5% consistency with recycled oxygen stage filtrate. Discharge is accomplished by a rotating conical screw and agitating arms.

The system is exemplified by those in operation at Eddy Forest Products in Espanola, Ont. and at the Franklin, Va. mill of Union Camp Corp. (30). The Eddy installation is shown schematically in Fig. 4 (32). Washed unbleached pulp is dewatered to a consistency of about 30% in a twin roll press. Magnesium sulfate, alkali and steam are then added,

and the pulp is fed to the reactor. White liquor is used as the alkali source for reasons of economy and to maintain the mill's sodium and sulfur balances. It must, however, first be oxidized, since the sulfide ion would otherwise lead to a loss of selectivity in the oxygen stage. This is accomplished by contacting air or oxygen with the liquor in a separate vessel. Steam may or may not be added to the reactor itself, depending on the extent of delignification (and corresponding heat of reaction) and the retention time available. A typical set of conditions within the reactor would include: pressure 0.62 MPa (80% oxygen, 20% steam) and temperature 110°C at a retention time of 30 min. Upon entering the reactor, the pulp passes through a fluffing mechanism and falls onto the bed. The bed level is sensed by a nuclear gage and is controlled by changing the flow rate of the leaving stream.

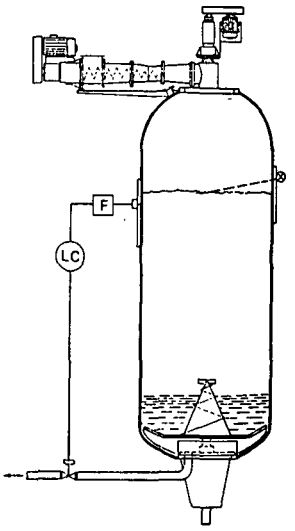

Figure 3. MoDo-CIL reactor (33).

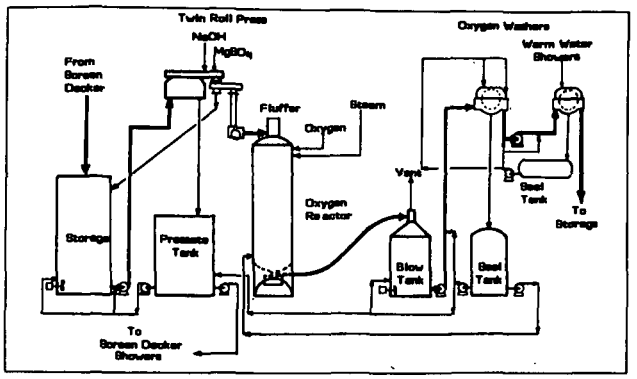

Figure 4. Typical oxygen bleaching system (32).

In the high-consistency systems, the possibility of ignition of combustible gases is rendered insignificant by taking simple precautions. Concentrations of carbon monoxide, methanol and turpentine in the reactor are monitored, and care is taken to ensure that volatile additives (e.g., some defoamers) do not enter the reactor with the pulp. The usual safety devices include an automatic relief valve, rupture discs and temperature-controlled quench showers. The concentration of combustible gases is controlled, usually by maintaining a continuous bleed stream. Some installations (31) are equipped with a catalytic system for carbon monoxide destruction, which obviates the need for venting the reactor.

The Sapoxal process (35-38) is inherently similar to the MoDo-CIL process, but operates at somewhat lower consistencies (17-25%), for which the reactor is especially designed. As illustrated in Fig. 5, it contains a series of trays, arranged one above the other. Each tray is divided into twelve compartments by radial walls and each has a cutout which coincides with the cross-section of the compartments. The trays, but not the walls, rotate, with the result that each compartment is emptied into the one below, once per revolution. The retention time of the pulp can thus be varied by varying the speed of rotation and is, within limits, independent of the production rate. Bed compaction, which tends to become more pronounced as the consistency is decreased, is avoided, since the bed depth is never greater than the distance between trays.

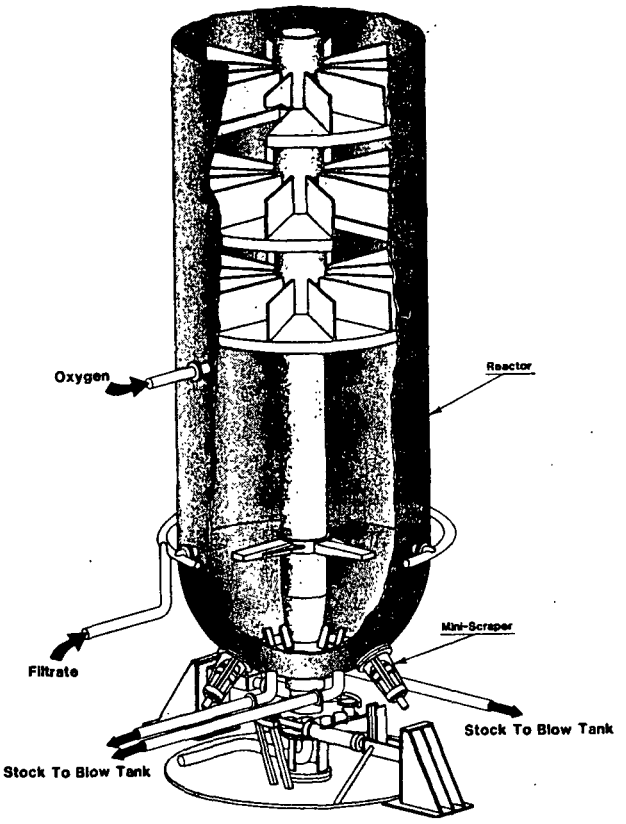

Figure 5. Bottom section of reactor used for the Sapoxal process (Kamyr Inc.).

Advantages claimed for operating at the lower consistencies that this arrangement permits are low bed combustibility and a lowering of the temperature rise associated with the reaction exotherm.

Other advantages claimed are better control of retention time due to the absence of channelling, and a more uniform gaseous atmosphere. It is apparently possible to operate these reactors without a bleed stream for combustible gas removal.

THE MEDIUM CONSISTENCY PROCESS

Decreasing the consistency of the pulp mass into the 8-16% range increases the amount of water available to dissolve the oxygen required for the delignification reaction. However, the amount of water present is still insufficient to dissolve all of the oxygen required, so the medium consistency processes provide for the production of a fine dispersion of oxygen bubbles in the pulp by intensive mixing. This has only become possible in the last few years, with the introduction of medium consistency mixing technology.

After the oxygen is dispersed in it, the pulp is transferred to a reactor, in which the delignification reaction is allowed to continue. The dispersions are relatively stable and the buoyancy imparted by the trapped oxygen reduces the likelihood of bed compaction that exists at high consistency. No special dewatering equipment is needed to operate in the medium consistency range.

Processes operating in the 8-16% consistency range have been described by, among others, Kamyr (39, 40), Impco (41), Sunds Defibrator (42,43), and Rauma Repola (44). Enz and Emmerling (41) have recently provided a detailed description of a typical system, for which the flow sheet is shown in Fig. 6. Partially washed pulp from the blow tank of a continuous digester is pumped via a knotter to a pressure washer, where it is washed with filtrate from the post-oxygen washer. Dilution liquor, caustic and steam are added to the pulp as it leaves the washer. A thick stock pump then feeds the pulp at 13% consistency to a high shear mixer that fluidizes the pulp and disperses oxygen in it. The mixture of pulp, caustic and oxygen, at 94 degrees C, then passes to an upflow reactor. The reactor has a high aspect ratio, being 2.75 m in diameter and 27.9 m high, to prevent channeling. It is designed for 45 minutes retention at 420 kPa, and is constructed of 316L clad stainless steel.

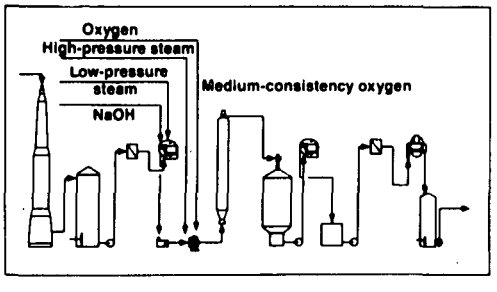

Figure 6. Typical medium consistency oxygen delignification system (41).

At the top of the reactor, the stock is diluted to 10% consistency before being moved toward a central discharge housing by a rotating plow-type discharger. It is then blown to a vertical pipe on top of the blow tank that is equipped with an induced draft fan to purge the tank of entrained gases. Stock from the blow tank passes to a pressure washer, where it is washed with filtrate from the screened pulp washer. The washed stock is diluted, screened, and sent to the screened pulp washer, where it is further washed with combined condensate and fresh water. From there it goes to a 3-stage C/D-(EO)-D bleach plant.

In operation, this system has allowed the production of the bleach plant to be increased from 320 to 410 tons/day with no change in pulp strength and improvements in final brightness and brightness stability. No magnesium salts or other carbohydrate protectors are used.

Although normally designed for pressurized operation, medium consistency systems incorporating open towers are also being used. These are sometimes referred to as hydrostatic systems since the only pressure supplied is the hydrostatic head represented by the column of pulp in the reactor. They are normally found in sulfite mills, but are also capable of delignifying kraft pulps, especially hardwoods, to modest degrees (about 30%).

The trend in new installations is strongly toward the medium consistency process. According to a 1987 review of 19 new systems started up or slated for startup in the period 1985-1989, all but one are medium consistency. Among the reasons that may be cited for this trend (39-45) are lower capital, greater ease of stock handling with the new medium consistency mixing and pumping technology, improved selectivity, and freedom from hazards associated with a continuous oxygen-rich vapor phase. On the other hand, chemical consumption is higher than in the high consistency systems and longer retention times are needed for the same degree of delignification.

Proponents of the high consistency systems claim that the advantages of the newer system are overstated. The difference in investment is due mainly to a simpler feeding system and elimination of a press upstream of the reactor. However, to maintain the same level of preoxygen washing, the medium consistency system would require an extra washer to replace the press, lessening the advantage. Laboratory data indicate no difference in selectivity at the same level of magnesium addition (46) and the chemical consumption difference may be significant. In summary, both process types should be considered for any new installation.

PROCESS VARIABLES

The response of the oxygen bleaching system to changes in process variables is a manifestation of the kinetics of the component chemical reactions and mass-transfer processes. Kinetic studies such as that of Olm and Teder (24) therefore provide a useful framework for predicting these effects and rationalizing observations such as those made by Hartler et al. in their process variable studies (47).

Time and Temperature

At fixed alkali concentration, the decrease of kappa number with time exhibits two distinct phases,

both of which are first order rate processes. There is an initial rapid drop followed by a slower one. This is interpreted as being due to the presence of two types of lignin which differ in ease of removal. The two delignification phases are directly paralleled by two corresponding cellulose depolymerization phases.

A consequence of the first-order nature of the delignification process is that, given enough alkali, the kappa number will continue to drop indefinitely. This is in contrast to the normal observation that the process appears to stop when a limiting kappa number is reached, as shown in Fig. 7 (47). The latter behavior results when the alkali charge is exhausted. Figure 7 also serves to show that delignification is considerably accelerated by an increase in temperature; the point of alkali exhaustion is reached much more rapidly at 130° than 85°.

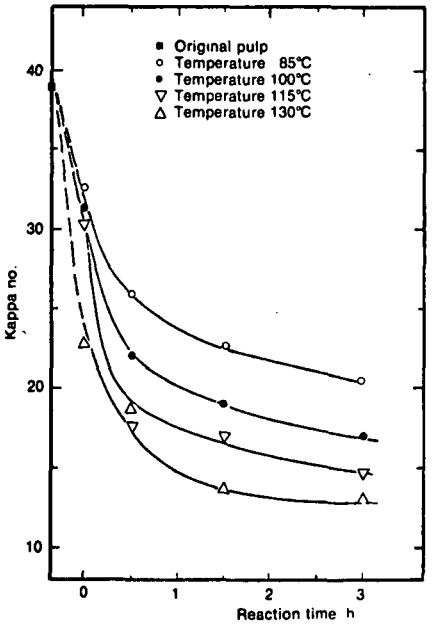

Figure 7. Effect of temperature on oxygen delignification rate. Conditions: 3.2% NaOH (o.d. pulp basis), 0.5 mPa total pressure, 20% consistency (47).

As shown in Fig. 2, the parallel between the rates of delignification and carbohydrate degradation results in a good correlation between viscosity and kappa number. This relationship tends to be fairly independent of process variables, although selectivity does suffer if the temperature is increased beyond about 120 degrees C, or if all of the alkali is consumed.

Alkali Charge

Both delignification and cellulose degradation are substantially accelerated by increased alkali concentration and therefore by increased alkali charge at constant consistency. This is illustrated by Fig. 8 (46).

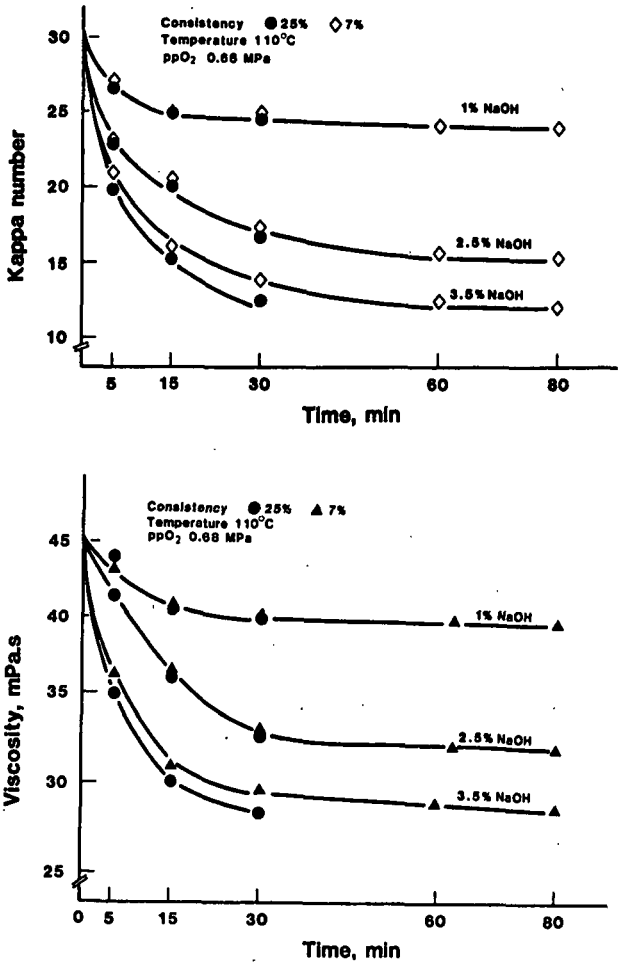

Figure 8. Effects of time, NaOH charge and consistency on kappa number and viscosity. Initial kappa number 30.6; initial viscosity 44 mPa.s (46).

Oxygen Pressure

In general, the effect of oxygen pressure (2-15 atm) is small in comparison to the effects of alkali charge and temperature (47). On the other hand, the kinetic studies already referrred to (24-26) show that oxygen pressure has an appreciable effect on the observed rates at constant alkali concentration. The apparent departure of observed behavior from theoretical predictions is due to the fact that alkali is normally the limiting reactant, oxygen being present in excess. In the presence of insufficient alkali, increases in oxygen pressure will have relatively little effect.

Consistency

In spite of its far-reaching process implications, the effect of consistency at fixed alkali charge is relatively small. Lowering the consistency results in a moderate slowing down of both the delignification and carbohydrate degradation reactions, as a result of the associated decrease in alkali concentration.

SYSTEMS ASPECTS

The effects of installing an oxygen delignification stage extend far beyond the bleach plant (48,49). The operation, and in some cases even the design, of other equipment will be affected in significant ways that must be considered before the change is made. The areas affected include screening, brown stock washing, chemical and heat recovery, downstream bleaching, stock preparation and wastewater treatment.

Placement of the Oxygen Stage

If an oxygen stage is to be used for predelignification, it is most logically integrated into the brown stock washing system. Good upstream washing is essential, since black liquor solids both consume oxygen and damage selectivity. Good downstream washing is necessary to fully realize the pollution abatement potential of the stage. Oxygen stage washer filtrate is used as wash liquor in the brown stock system and thus finds its way back to the recovery system. Oxygen stage washer losses enter the chlorination stage and become unrecoverable.

Placing the oxygen stage in the brown stock washing area necessitates closing the screen room water circuit to avoid the loss of oxygen stage solids. The resulting potential for foaming problems normally dictates the use of pressure screens.

Oxygen predelignification is usually limited to removal of about 50% of the lignin in the unbleached pulp, to avoid pulp strength loss. The subsequent chlorination stage would be conducted at high temperature because of the normally high temperature of the pulp leaving the oxygen stage washers. Addition of chlorine dioxide thus becomes necessary and the metallurgy of the chlorination washer must be appropriate.

Implications for the Recovery System

If pure sodium hydroxide were used as alkali in the oxygen stage, the amount added, together with the ClO_2 generator spent acid, would probably exceed the requirement for sodium make-up to the liquor system. For this reason, oxidized white liquor is usually used as an alkali source. If white liquor were used to satisfy the total alkali requirements of the oxygen stage, an increase of about 7% in the capacity of the causticizing and lime reburning systems would be needed.

The additional water added with the alkali and as direct steam in the oxygen stage amounts to about 0.4 kg/kg pulp. A corresponding increase in evaporator capacity would be required. Alternatively, washing capacity could be added to allow a coresponding decrease in the dilution factor.

Recycling of organic material dissolved in the oxygen stage to the recovery furnace typically increases the load on that unit by 3-5%.

SUMMARY

In the past fifteen years, oxygen bleaching has become an important pulp processing technology. This came about as a result of the need for environmental improvements, the discovery of the protective action of magnesium ion, and identification of appropriate operating conditions.

The problem of oxygen transfer within a three-phase system was first solved by removing most of the free liquid phase, giving rise to the high consistency process. This is now well established but has been challenged by the medium consistency process, which offers potential capital cost advantages and makes use of recently introduced gas-liquid mixing technology.

Current research is leading to a better fundamental understanding of the behavior of oxygen bleaching systems. This knowledge may be expected to result in further improvements in the technology.

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